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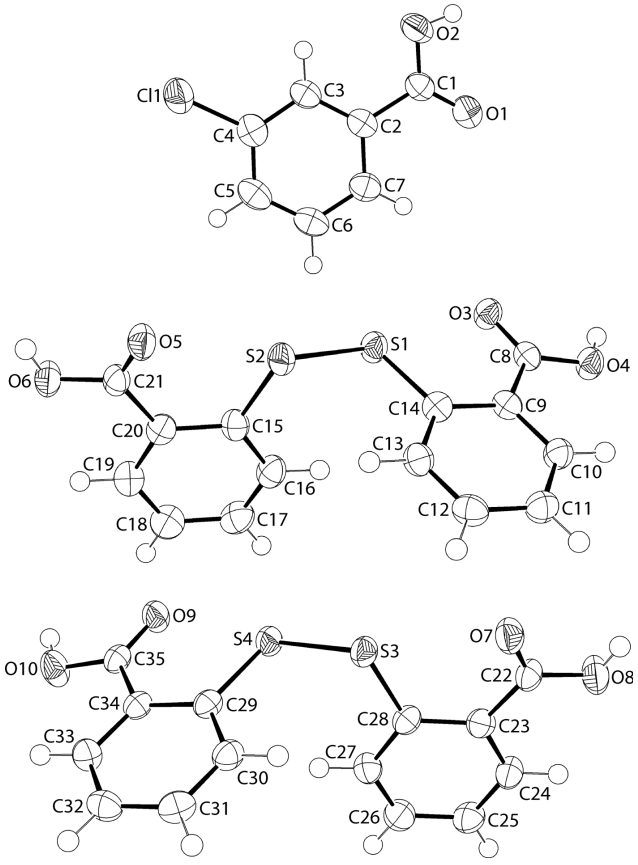
Crystal structure of the co-crystal 2-[(2-carboxyphenyl)disulfanyl]benzoic acid – 3-chlorobenzoic acid (2/1), $C_{35}H_{25}ClO_{10}S_4$



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Abstract

$C_{35}H_{25}ClO_{10}S_4$, triclinic, $P\bar{1}$ (no. 2), $a = 7.9798(2)$ Å, $b = 10.2392(3)$ Å, $c = 20.6956(4)$ Å, $\alpha = 103.632(2)°$, $\beta = 96.082(2)°$, $\gamma = 96.053(2)°$, $V = 1619.13(7)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0493$, $wR_{ref}(F^2) = 0.1413$, $T = 100(2)$ K.

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The molecular structure is shown in the figure. Tables 1 and 2, respectively, contain details on crystal characteristics and measurement conditions, and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.09 × 0.07 × 0.04 mm
Wavelength:	Cu $K\alpha$ radiation (1.54178 Å)
μ:	3.99 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	76.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	36982, 6563, 0.029
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 6113
$N(param)_{refined}$:	471
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

The title co-crystal was prepared through solvent drop grinding of 2-mercaptobenzoic acid (2-MBA; Merck) and 3-chlorobenzoic acid (ClBA; Merck) in a 1:1 molar ratio (0.001 mol, 0.154 g for 2-MBA and 0.157 g for ClBA). The mixture was ground for 15 min in the presence of few drops of methanol; the procedure was repeated three times. Colourless block crystals were obtained by carefully layering benzene (1.5 mL) on a dichloromethane (1.5 mL) solution of the ground co-crystal. M.p. (Hanon MP-450): 448.4–451.8 K. IR (Bruker Vertex 70v; cm^{-1}): 3074–2819(w) ν(C—H), 1675(s) ν(C = O), 1597(s) and 1468(m) ν(C = C), 1414(s) δ(C—H), 740(s) δ(C—Cl).

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$. The O-bound H-atoms were located in difference Fourier maps but were refined with a distance restraint of O—H = 0.84 ± 0.01 Å, and with $U_{iso}(H)$ set to $1.5U_{eq}(O)$. Owing to poor agreement, three reflections, i.e. ($\bar{1}$ $\bar{6}$ 3), ($\bar{9}$ $\bar{4}$ 5) and ($\bar{9}$ $\bar{4}$ 6), were omitted from the final cycles of refinement.

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
Cl1	0.99576(11)	0.78924(9)	0.30664(4)	0.0374(2)
O1	0.7090(3)	0.5151(3)	0.00324(12)	0.0370(6)
O2	0.5573(3)	0.5863(3)	0.08599(13)	0.0342(5)
H2O	0.480(8)	0.551(8)	0.054(3)	0.16(4)*
C1	0.6993(4)	0.5720(3)	0.06257(16)	0.0258(6)
C2	0.8567(4)	0.6284(3)	0.11016(16)	0.0244(6)
C3	0.8490(4)	0.6768(3)	0.17820(16)	0.0259(6)
H3	0.7429	0.6755	0.1951	0.031*
C4	0.9988(4)	0.7269(3)	0.22069(16)	0.0285(7)
C5	1.1553(4)	0.7277(3)	0.19732(18)	0.0312(7)
H5	1.2571	0.7611	0.2276	0.037*
C6	1.1614(4)	0.6795(3)	0.12970(18)	0.0310(7)
H6	1.2680	0.6804	0.1132	0.037*
C7	1.0129(4)	0.6296(3)	0.08563(17)	0.0285(6)
H7	1.0175	0.5965	0.0390	0.034*
S1	0.78621(9)	0.40830(7)	0.26149(3)	0.02272(17)
S2	0.81972(9)	0.50572(7)	0.36157(3)	0.02302(17)
O3	0.7184(3)	0.3119(2)	0.12761(10)	0.0232(4)
O4	0.9046(3)	0.2609(2)	0.05497(10)	0.0246(4)
H4O	0.817(4)	0.233(5)	0.0272(18)	0.056(14)*
O5	0.7639(3)	0.6263(2)	0.48620(10)	0.0248(4)
O6	0.6717(3)	0.5185(2)	0.56095(10)	0.0260(5)
H6O	0.650(5)	0.5964(19)	0.5773(19)	0.037(11)*
C8	0.8664(4)	0.3090(3)	0.11575(13)	0.0192(5)
C9	1.0138(4)	0.3573(3)	0.16869(14)	0.0194(5)
C10	1.1782(4)	0.3535(3)	0.15064(14)	0.0222(6)
H10	1.1918	0.3223	0.1047	0.027*
C11	1.3216(4)	0.3944(3)	0.19857(15)	0.0253(6)
H11	1.4322	0.3925	0.1857	0.030*
C12	1.3005(4)	0.4381(3)	0.26537(15)	0.0247(6)
H12	1.3977	0.4642	0.2986	0.030*
C13	1.1398(4)	0.4443(3)	0.28459(14)	0.0233(6)
H13	1.1283	0.4760	0.3307	0.028*
C14	0.9944(4)	0.4043(3)	0.23691(14)	0.0207(6)
C15	0.8330(4)	0.3744(3)	0.40463(14)	0.0211(6)
C16	0.8839(4)	0.2504(3)	0.37377(15)	0.0249(6)
H16	0.9135	0.2366	0.3296	0.030*
C17	0.8916(4)	0.1483(3)	0.40669(16)	0.0291(7)
H17	0.9244	0.0644	0.3846	0.035*
C18	0.8522(4)	0.1664(3)	0.47164(17)	0.0297(7)
H18	0.8585	0.0959	0.4942	0.036*
C19	0.8031(4)	0.2894(3)	0.50334(16)	0.0271(6)
H19	0.7759	0.3026	0.5478	0.033*
C20	0.7933(4)	0.3934(3)	0.47070(14)	0.0215(6)
C21	0.7417(4)	0.5228(3)	0.50620(14)	0.0213(6)
S3	0.53104(9)	0.89128(7)	0.74390(3)	0.02117(16)
S4	0.56090(9)	1.00475(7)	0.84118(3)	0.02130(16)
O7	0.5967(3)	0.7603(2)	0.61967(10)	0.0255(4)
O8	0.6858(3)	0.8659(2)	0.54392(11)	0.0305(5)
H8O	0.708(6)	0.787(2)	0.529(2)	0.066(16)*
O9	0.6257(3)	1.1438(2)	0.96992(10)	0.0255(5)
O10	0.4396(3)	1.2103(2)	1.03995(10)	0.0299(5)
H10O	0.532(3)	1.235(5)	1.0652(19)	0.057(14)*
C22	0.6135(4)	0.8625(3)	0.59818(14)	0.0212(6)
C23	0.5560(4)	0.9908(3)	0.63037(14)	0.0208(6)
C24	0.5439(4)	1.0907(3)	0.59503(15)	0.0247(6)
H24	0.5782	1.0759	0.5516	0.030*
C25	0.4830(4)	1.2109(3)	0.62180(15)	0.0265(6)
H25	0.4757	1.2781	0.5972	0.032*
C26	0.4331(4)	1.2311(3)	0.68499(16)	0.0272(6)
H26	0.3905	1.3128	0.7038	0.033*
C27	0.4444(4)	1.1336(3)	0.72139(15)	0.0240(6)
H27	0.4080	1.1491	0.7645	0.029*
C28	0.5084(4)	1.0133(3)	0.69551(14)	0.0203(6)
C29	0.3519(4)	1.0168(3)	0.86387(14)	0.0197(5)
C30	0.2075(4)	0.9642(3)	0.81723(14)	0.0223(6)
H30	0.2198	0.9220	0.7722	0.027*
C31	0.0457(4)	0.9726(3)	0.83558(15)	0.0245(6)
H31	−0.0513	0.9372	0.8029	0.029*
C32	0.0246(4)	1.0321(3)	0.90117(16)	0.0251(6)
H32	−0.0863	1.0349	0.9138	0.030*
C33	0.1658(4)	1.0873(3)	0.94788(15)	0.0229(6)
H33	0.1514	1.1295	0.9926	0.027*
C34	0.3309(4)	1.0821(3)	0.93034(13)	0.0188(5)
C35	0.4784(4)	1.1473(3)	0.98131(13)	0.0194(5)

Comment

Owing to the presence of a central disulphide bond, 2-[(2-carboxyphenyl)disulfanyl]benzoic acid (2,2′-dithiobenzoic acid; DTBA), is a flexible dicarboxylic acid. This conformational flexibility is emphasized in a recent report of a tri-polymorphic inclusion compound formed between DTBA and trimethylamine [5]. Indeed, most studies of DTBA are motivated by co-crystal formation and it is of interest that sometimes DTBA found in co-crystals is a product of co-crystallisation experiments starting with 2-mercaptobenzoic acid (2-MBA) [6, 7] whereby 2-MBA is oxidised to DTBA. As a continuation of studies in this area [6, 8, 9], the title co-crystal was isolated from the attempted 1:1 co-crystallisation experiments between 2-MBA and a second carboxylic acid, namely 3-chlorobenzoic acid (3-ClBA).

X-ray diffraction showed the asymmetric unit in title co-crystal comprises two independent molecules of DTBA and one of 3-ClBA, indicating oxidation of 2-MBA had occurred during co-crystal formation. Confirmation that the molecule of 3-ClBA exists as a carboxylic acid is readily seen in the pattern of C1—O1, O2 bond lengths, i.e. 1.243(4) Å and 1.288(4) Å. A small twist from planarity is noted in the molecule. The r.m.s. deviation from the least-squares plane through the ring-carbon and chloride atoms being 0.0036 Å, and the dihedral angle between this plane and that through the carboxylic acid residue is 7.55(16)°. The crystal structure of 3-ClBA was originally reported in 1975 with a low temperature (105 K) redetermination of this $P2_1/c$ polymorph [11] subsequently complimented by the report of a $C2/c$ polymorph [12].

The comparable dihedral angles between C_6/CO_2 in these structures are 4.1(4)° [11] and 5.8(2)° [12].

The conformations of the two DTBA molecules comprising the asymmetric unit resemble each other as seen in the respective r.m.s. bond and angle fits of 0.0054 Å and 0.491° for the inverted-S1 and S3-molecules [13]; each lacks crystallographically imposed symmetry. The patterns in the C—O(hydroxy), O(carbonyl) bond lengths are consistent with the presence of carboxylic acid residues. The C_6/CO_2 dihedral angles are 3.7(3)° [O3-residue], 14.7(2)° [O5], 14.0(2)° [O7] and 4.1(2)° [O9]. This effectively co-planar relationship coupled with the observation each carbonyl-O atom is orientated towards the adjacent disulphide-S atom is indicative of attractive, hypervalent S ← O interactions [14]. The shortest such interaction in the present co-crystal structure is 2.675(2) Å for S4···O9 and the longest, 2.737(2) Å, for O3···O7. The twists in the molecules is best indicated by the C14—S1—S2—C15 and C28—S3—S4—C29 torsion angles of −91.06(15)° and 87.15(15)°, respectively, and the dihedral angles between the two phenyl rings in the S1- and S3-molecules, i.e. 79.54(11)° and 80.76(11)°, respectively. The crystal structure of the parent DTBA molecule has been determined and shows the asymmetric unit to comprise one and a half molecules, with the latter disposed about a 2-fold axis of symmetry [15]. The comparable C—S—S—C torsion and C_6/CO_2 dihedral angles are 86.12(14)° and 74.66(8)° for the molecule in the general position, and 87.90(13)° and 77.55(8)° for the symmetric molecule.

In the molecular packing, two distinct aggregation patterns based on conventional hydroxy-O—H···O(carbonyl) hydrogen bonding are discerned, each resulting in an eight-membered $\{\cdots HOCO\}_2$ synthon. In the first of these, centrosymmetrically-related two-molecule aggregates of 3-ClBA are formed [O2—H2o···O1^{i} = 1.78(7) Å, O2···O1^{i} = 2.608(4) Å with angle at H2o = 170(7)° for symmetry operation i: $1-x$, $1-y$, $-z$]. The second aggregate is a twisted, supramolecular chain comprising alternating S1- and S3-molecules [O4—H4o···O9^{ii} = 1.84(4) Å, O4···O9^{ii} = 2.665(3) Å with the angle at H4o = 170(5)°; O6—H6o···O7: 1.82(3) Å, 2.648(3) Å and 175(3)°; O8—H8o···O5: 1.80(3) Å, 2.633(3) Å and 171(4)°; O10—H10o···O3^{iii}: 1.84(3) Å, 2.663(3) Å and 171(3)°, for ii: x, $-1+y$, $-1+z$ and iii: x, $1+y$, $1+z$]. The chain is orientated along [0 1 1]. Connections between the aggregates mediated by hydrogen bonding include π-stacking interactions between (C2—C7)···(C9—C14) and (C2—C7)···(C29—C34)^{iv} phenyl rings with ring-centroid separations of 3.6865(18) and 3.7344(18) Å, respectively. These interactions indicate the 3-ClBA molecule effectively bridges two independent DTBA molecules. The packing also features several parallel C=O···π interactions [16, 17] with C21=O5···π(C15—C20) presenting the shortest O···ring-centroid contact of 3.299(3) Å; the angle at O5 is 96.85(19)°.

Co-crystals of 3-ClBA with other carboxylic acids have not been reported and the sole example of a carboxylic acid co-crystal of DTBA is its 1:1 co-crystal with 2-MBA [7]. In the structure of this co-crystal, two DTBA molecules associate *via* hydroxy-O—H···O(carbonyl) hydrogen bonds leaving each of the outer carboxylic acid groups free to form eight-membered synthons with a 2-MBA molecule to result in the formation of a four-molecule aggregate.

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